

THEORY OF INDIRECT EXCHANGE INTERACTION IN SPINEL-LIKE SYSTEMS*

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ABSTRACT. A theoretical study of the indirect exchange interaction for the spin coupling in spinel type magnetic compounds is made on the basis of a mechanism suggested by us recently. Detailed calculations are carried out for the elementary, four-centre (A-O-B₂; A and B represent the cations and O denotes the anion) and five-electron system. This furnishes the appropriate model for describing both A-B and B-B types of interactions.

The relative energies of the ferromagnetic (Quartet Q) and the two ferrimagnetic (Doublets D₁ and D₂) states are assessed for the above model. It is shown that, within the framework of the present mechanism, the ferrimagnetic state D₁, which represents antiparallel spins in A-B and parallel in B-B, is the most stable state. This is in agreement with the observed situation.

1. INTRODUCTION

Some recent papers (Anderson, 1959; Koide, Sinha and Tanabe, 1959) on superexchange interaction have led to a reappraisal of the types of mechanisms responsible for the spin coupling of magnetic ions in certain magnetic compounds (see also Kanamori, 1959; Keffer and Oguchi, 1959). It seems that of the various mechanisms proposed some are only apparently distinct and others embrace complementary features of the physical situation. However, it remains to establish as to which of these play the dominant role.

One of these mechanisms, which is analogous to spin-polarization around a nucleus that leads to nuclear indirect exchange was recently suggested by us (Koide, Sinha and Tanabe, 1959). It constitutes an important spin dependent effect and the contributions due to this mechanism needs to be fully assessed for each type of crystal structure while discussing the magnetic properties of such compounds. The previous paper, in addition to dealing with the general formulation of the mechanism in terms of semi-localized orbitals for the anion electrons, furnishes a quantitative calculation for the collinear three centre and four electron system applicable to magnetic compounds having rock salt or perovskite type structures. In another paper (Sinha and Koide, 1960), we have given a theoretical study of this interaction by choosing an elementary unit

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which is appropriate for zinc-blends type structures. In the present paper we give an analysis of the indirect exchange interactions in spinel-like systems, using, as in our previous papers, the Heitler-London method with the inclusion of the correlation effect which involves spin dependent transitions of the anion electrons.

2. THEORETICAL MODEL

It is appropriate to discuss briefly the relevant features of spinel structure before coming to the model chosen for calculation (for a fuller description of the structure see Gorter, 1954). The ideal spinel structure can be described as a cubic close packed lattice of anions (e.g., O^{2-}) with metal ions partly filling the tetrahedral (half of the 16 A sites) and the octahedral (half of the 32 B sites) interstices. There are eight molecules in the cubic unit cell, the molecular formula being AB_2O_4 . The immediate environment of each metal ion is thus cubic. The oxide ion, however, has four nearest neighbour metal ions of which three are at octahedral (B) sites and the fourth is in a tetrahedral (A) site. The three octahedral cations are situated at a distance R_o along three mutually perpendicular directions from the oxide ion. The tetrahedral cation is in the $\langle 111 \rangle$ direction at a distance R_t and away from the octant which contains the three octahedral cations. The immediate symmetry around the oxide ion i.e., of the unit A-O-B₃ is described by the point group C_{3v} ; the next nearest neighbours of this oxide ion are twelve oxide ions of the face centred cubic lattice.

According to Neel's (1948) phenomenological theory for ferrospinel, there are three types of negative interactions, namely A-A, B-B and A-B, the relative strengths of which determine the ultimate coupling; assuming, of course, the presence of one kind of magnetic ion (e.g., Fe^{3+}) only. If the AB interaction is much stronger than A-A and B-B interactions, the spin ordering $\vec{A} [\vec{B}_2]$ is favoured. This constitutes the fundamental assumption of the two sub-lattice model of Neel. However, when either of A-A and B-B interaction is comparable with A-B interaction, further generalizations as envisaged by Yafet and Kittel (1952) by dividing A into two sub-lattices A_1 and A_2 and B into four sub-lattices B_1 , B_2 , B_3 and B_4 , have to be considered. These considerations lead to certain triangular arrangements of the spin vectors associated with the sub-lattices.

The strengths of these interactions would depend on the nature and mechanism of the fundamental types of indirect exchange interactions involving the anion lattice as well as the cation-anion-cation angles and cation-cation and cation-anion distances. Aside from qualitative discussions (Wollan, 1960), no non-empirical analysis of such indirect exchange interactions in spinel-like systems has been made. In what follows, we consider a detailed calculation for one of the mechanisms suggested before, on the basis of an appropriate model chosen.

In view of the large A-A distance and unfavourable angles, we shall disregard the study of the A-A interaction. As is supported by experimental results this interaction, in any way, is too feeble. The problem then is to select a model which includes the effect of both A-B and B-B interactions. Although we shall always keep the unit A-O-B₃ (with C_{3v} symmetry) in mind, we choose a still smaller unit, namely, A-O-B₂, which furnishes the appropriate model for describing both types of interactions. At times, while considering the symmetry of orbitals involved in the study, we shall refer to the complete unit having C_{3v} symmetry. If the O²⁻ ion in the unit A-O-B₂ was in the plane of A-B₂, the symmetry of A-O-B₂ would have been taken as C_{2v} . Since, O²⁻ is slightly below this plane, this symmetry is lost. However, we shall make use of some symmetry planes even for this unit in order to classify the orbitals and to study the nature of wavefunctions. The geometry of the unit is shown in Fig. 1.

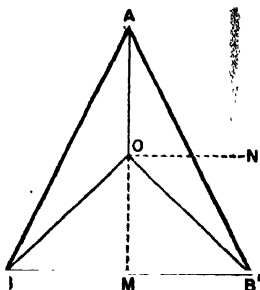


Fig. 1

3. THE WAVE FUNCTIONS OF THE CATION ELECTRONS

We consider one representative electron each from the three magnetic ions i.e., one at the tetrahedral site A, and the other two at the octahedral sites B and B'. Each electron is assumed to be coupled strongly by intraatomic spin dependent interaction while moving in the field of their respective ion cores. Only one type of magnetic ions are considered for simplicity with d^5 electronic configuration and in ${}^6S_{5/2}$ state e.g., Fe³⁺.

We denote the orbital functions of the electrons of the two octahedral cations by u_1 and u_2 and that of the tetrahedral cation by v . In the choice of the explicit forms of these orbitals, we shall be guided by their degree of overlap with the anion orbitals, and the splitting of the d orbitals in the crystal field. It is well known that in the cubic field due to octahedrally situated six surrounding ions the $3d$ level of the magnetic ion splits up into lower triplets (t_{2g}) and the upper doublets (e_g), the triplets being d_{xy} , d_{yz} and d_{zx} and the two doublets being $d_{x^2-y^2}$ and d_{z^2} . When the cations are tetrahedrally surrounded by the anions, the situation is reversed and the triplets are higher than the doublets.

If the three cartesian axes are taken to be the lines joining the anion to the three octahedral cations, then the obvious choice for u_1 and u_2 would be one of the e_g orbitals, in particular, the d -function having axial symmetry with respect to the bonds BO and B'O (see Fig. 1). For v one can take the appropriate t_{2g} orbital. Any other choice of axes (e.g., A O as the z axis and x parallel to BB' and passing through O) would not make any difference in the calculations presented below in that the orbitals can be re-expressed by suitable transformations. Thus we assume the following behaviour of u_1 , u_2 and v under reflection in the plane AM normal to the figure (Fig. 1).

$$u_1 \longleftrightarrow u_2 \quad \text{and} \quad R_{AM}v = v$$

where R_{AM} denotes the corresponding operation. Switching over to the condition $R_{AM}v = -v$ would not bring about any difference in the physical arguments involved in the calculations.

Including the spin functions, we shall have eight Slater determinants for the three cation electron system. We shall choose such linear combinations of these which are eigenstates of the S^2 operator. We have one quartet and two doublet states. These are given below :

$$|^4\Phi_{od}(M_s = \frac{3}{2})>_c = [u_1u_2v] \quad \dots (3.1)$$

$$|^2\Phi_{od}(\frac{1}{2})>_c = \{[u_1\bar{u}_2v] + [\bar{u}_1u_2v] - 2[u_1u_2\bar{v}]\} / \sqrt{6} \quad \dots (3.2)$$

$$|^2\Phi_{ev}(\frac{1}{2})>_c = \{[u_1\bar{u}_2v] - [\bar{u}_1u_2v]\} / \sqrt{2} \quad \dots (3.3)$$

Here the bracket notation represents the usual Slater determinant multiplied by $(N!)^{-1}$ (in this case $(3!)^{-1}$). The orbitals without bar include up spin and with bar down spin functions of the electrons in them. The suffix c outside the kets refers it with respect to cation electrons and the suffixes od or ev denote that the states are odd or even under the operation R_{AM} .

The classification of the states with respect to the symmetry operation R_{AM} has the following advantage. The quartet $|^4\Phi_{od}>_c$, of course, would represent the ferromagnetic state. The ferrimagnetic state $|^2\Phi_{od}>_c$ represents the situation where the spins in A and B are antiparallel, while that of BB are parallel. In effect, this would represent a dominant negative A-B interaction. The state $|^2\Phi_{ev}>_c$, however, represents the reverse situation with antiparallel spins of BB and parallel spins of AB. This represents the case with stronger B-B interaction. The picture remains incomplete unless the effect of anion electrons is included.

4. THE WAVE FUNCTIONS OF THE ANION ELECTRONS

Unlike our previous papers, where for anion electrons semilocalized orbitals are used, we shall follow a perturbation procedure right through in the present

formulation. We consider two anion electrons which play the dominant role in our mechanism. The appropriate $2p$ orbitals of the anion (e.g., O^{2-}) are no longer degenerate in the crystal field for the unit $A-O-B_3$ with C_{3v} symmetry. For the choice of axes along the three octahedral cations, the crystal field VC_{3v} gives rise to one non-degenerate orbital,

$$p_1(A_1) = \frac{1}{\sqrt{3}}(p_x + p_y + p_z) \quad \dots \quad (4.1)$$

belonging to A_1 representation of C_{3v} group and two degenerate orbitals, belonging to E representations i.e.,

$$\left. \begin{aligned} p_2(E) &= \frac{1}{\sqrt{2}}(p_x - p_y) \\ p_3(E) &= \frac{1}{\sqrt{6}}(2p_z - p_x - p_y) \end{aligned} \right\} \quad \dots \quad (4.2)$$

If, on the other hand, AO is taken as the z axis and ON as the x axis, it can be easily shown that p_z belongs to A_1 representation and its energy differs from the doubly degenerate orbitals p_x and p_y belonging to E representation. It is seen for both cases that the orbital belonging to A_1 representation has a larger overlap with the orbitals of the cation electrons.

We represent the zeroth order ground state for the anion system by considering the representative two electrons with coupled spins in the orbital belonging to A_1 representation. We denote this symbolically by ϕ . It may be added that for the restricted unit $A-O-B_3$ we shall replace p_1 (A_1) by

$$p_1 = (p_z + p_x)/\sqrt{2} \quad (4.3)$$

with OB as z axis and OB' as x in that the effect of p_y would be negligible. Thus our ϕ would represent p_1 as given by (4.3) or p_z depending on the choice of axes. In effecting the actual transformation the vector-like nature of the p orbitals should be taken into account.

The wave functions of the two anion electrons in the zeroth order ground state is expressed as

$$|^1\chi^{(0)}_{av} \rangle_a = [\phi\phi] \quad (4.4)$$

which is even under R_{AM} .

We defer the specific choice of excited orbitals until later sections and consider their effect in terms of some symmetry properties. It would suffice to consider the configurational interactions in terms of transitions to two types of orbitals, one even under R_{AM} and the other odd. They are respectively denoted by γ and η .

We have the following triplet states for the two anion electrons under consideration.

$$|^3\chi_{ev}>_a : \left\{ \begin{array}{l} [\phi\gamma] \\ \{[\phi\bar{\gamma}]+[\bar{\phi}\gamma]\}|\sqrt{2} \\ [\bar{\phi}\bar{\gamma}] \end{array} \right\} \quad \dots (4.5)$$

$$|^3\chi_{od}>_a : \left\{ \begin{array}{l} [\phi\eta] \\ \{[\phi\bar{\eta}]+[\bar{\phi}\eta]\}|\sqrt{2} \\ [\bar{\phi}\bar{\eta}] \end{array} \right\} \quad \dots (4.6)$$

Singlet states for the two anion electrons involving γ or η will have much higher energy than those described above and accordingly we omit them.

5. THE WAVE FUNCTIONS OF THE TOTAL SYSTEM

We first consider the zeroth order ground states of the total five electron and four centre system. The lowest state of the two anion electrons is $|^1\chi_{ev}>_a$ (cf. Eq. (4.4)) and hence the lowest ferromagnetic and two ferrimagnetic states are given by the products of (4.4) with (3.1), (3.2) and (3.3) respectively.

Ground states :

$$|^4\bar{\psi}_{od}^{(1)}> = ({}^4\bar{\Phi}_{od}^{(1)})_c ({}^1\chi_{ev}^{(0)})_a > = [u_1 u_2 v \phi \bar{\phi}] \quad \dots (5.1)$$

$$\begin{aligned} |^2\bar{\psi}_{od}^{(1)}> &= |({}^2\bar{\Phi}_{od}^{(1)})_c ({}^1\chi_{ev}^{(0)})_a > \\ &= \{[u_1 \bar{u}_2 v \phi \bar{\phi}] + [\bar{u}_1 u_2 v \phi \bar{\phi}] - 2[u_1 u_2 \bar{v} \phi \bar{\phi}]\} |\sqrt{6} \quad \dots (5.2) \end{aligned}$$

$$\begin{aligned} |^2\bar{\psi}_{ev}^{(1)}> &= |({}^2\bar{\Phi}_{ev}^{(1)})_c ({}^1\chi_{ev}^{(0)})_a > \\ &= \{[u_1 \bar{u}_2 v \phi \bar{\phi}] - [\bar{u}_1 u_2 v \phi \bar{\phi}]\} |\sqrt{2} \quad \dots (5.3) \end{aligned}$$

A large number of excited states for the total system is possible. These are the products of the cation states (3.1), (3.2) and (3.3) and the excited triplet states of the anion, namely, (4.5) and (4.6). We shall write down only those states which have the appropriate symmetry corresponding to the respective zeroth order ferromagnetic and ferrimagnetic states. Others with different symmetry are of no consequence in that they do not interact with the corresponding ground states described by (5.1) to (5.3). The excited states involving transitions to γ and η type orbitals are given below :

Excited States

Quartets

$$\begin{aligned} |^4\bar{\psi}_{od}^{\gamma_1}(\frac{1}{2})> &= \sqrt{\frac{2}{3}} |({}^4\bar{\Phi}_{od}^{(1)})_c ({}^3\chi_{ev}^{(1)})_a > - \sqrt{\frac{2}{3}} |({}^4\bar{\Phi}_{od}^{\frac{3}{2}})_c ({}^3\chi_{ev}^{(0)})_a > \\ &= \{2([u_1 u_2 v \phi \gamma] + [u_1 \bar{u}_2 v \phi \gamma] + [u_1 u_2 \bar{v} \phi \gamma]) \\ &\quad - 3([u_1 u_2 v \phi \bar{\gamma}] + [u_1 u_2 v \bar{\phi} \gamma])\} |\sqrt{30} \quad \dots (5.4) \end{aligned}$$

$$\begin{aligned}
 |^4\bar{\psi}_{od} \gamma^2(\frac{3}{2})\rangle &= |(^2\bar{\Phi}_{od}^{(1)})_o(^3\chi_{ov}^{(1)})_a\rangle \\
 &= \{2[u_1 u_2 \bar{v} \phi \gamma] - [u_1 \bar{u}_2 v \phi \gamma] - [\bar{u}_1 u_2 v \phi \gamma]\} / \sqrt{6} \quad \dots (5.5)
 \end{aligned}$$

Doublets

$$\begin{aligned}
 |^2\bar{\psi}_{od} \gamma^1(\frac{1}{2})\rangle &= \sqrt{\frac{6}{15}} |(^2\bar{\Phi}_{od}^{(1)})_o(^3\chi_{ov}^{(0)})_a\rangle - \sqrt{\frac{12}{15}} |(^2\bar{\Phi}_{od}^{(-1)})_o(^3\chi_{ov}^{(1)})_a\rangle \\
 &= \{([u_1 \bar{u}_2 v \phi \bar{\gamma}] + [u_1 \bar{u}_2 v \bar{\phi} \gamma] + [\bar{u}_1 u_2 v \phi \bar{\gamma}] + [\bar{u}_1 u_2 v \bar{\phi} \gamma]) \\
 &\quad - 2[u_1 u_2 \bar{v} \phi \bar{\gamma}] - 2[u_1 u_2 \bar{v} \bar{\phi} \gamma]) \\
 &\quad + (2[u_1 \bar{u}_2 \bar{v} \phi \gamma] + 2[\bar{u}_1 u_2 \bar{v} \phi \gamma] - 4[\bar{u}_1 \bar{u}_2 v \phi \gamma])\} / \sqrt{36} \quad \dots (5.6)
 \end{aligned}$$

$$\begin{aligned}
 |^2\bar{\psi}_{od} \gamma^2(\frac{1}{2})\rangle &= \sqrt{\frac{3}{8}} |(^4\bar{\Phi}_{od}^{(1)})_o(^3\chi_{ov}^{(-1)})_a\rangle - \sqrt{\frac{3}{8}} |(^4\bar{\Phi}_{od}^{(1)})_o(^3\chi_{ov}^{(0)})_a\rangle \\
 &\quad + \sqrt{\frac{3}{8}} |(^4\bar{\Phi}_{od}^{(-1)})_o(^3\chi_{ov}^{(1)})_a\rangle \\
 &= \{3[u_1 u_2 v \bar{\phi} \bar{\gamma}] - ([\bar{u}_2 u_2 v \phi \bar{\gamma}] + [\bar{u}_1 u_2 v \bar{\phi} \gamma] + [u_1 \bar{u}_2 v \phi \bar{\gamma}] \\
 &\quad + [u_1 \bar{u}_2 v \bar{\phi} \gamma] + [u_1 u_2 \bar{v} \phi \bar{\gamma}] + [u_1 u_2 \bar{v} \bar{\phi} \gamma]) \\
 &\quad + ([\bar{u}_1 \bar{u}_2 v \phi \gamma] + [\bar{u}_1 u_2 \bar{v} \phi \gamma] + [u_1 \bar{u}_2 \bar{v} \phi \gamma])\} / \sqrt{18} \quad \dots (5.7)
 \end{aligned}$$

$$\begin{aligned}
 |^2\bar{\psi}_{ov} \gamma^1(\frac{1}{2})\rangle &= \sqrt{\frac{2}{3}} |(^2\bar{\Phi}_{ov}^{(1)})_o(^3\chi_{od}^{(0)})_a\rangle - \frac{2}{\sqrt{6}} |(^2\bar{\Phi}_{ov}^{(-1)})_o(^3\chi_{od}^{(1)})_a\rangle \\
 &= \{[u_1 \bar{u}_2 v \phi \bar{\gamma}] + [u_1 \bar{u}_2 v \bar{\phi} \gamma] - [\bar{u}_1 u_2 v \phi \bar{\gamma}] - [\bar{u}_1 u_2 v \bar{\phi} \gamma] \\
 &\quad - 2[u_1 \bar{u}_2 \bar{v} \phi \gamma] + 2[\bar{u}_1 u_2 \bar{v} \phi \gamma]\} / \sqrt{12} \quad \dots (5.8)
 \end{aligned}$$

Excited states involving transition to η type orbital.

Quartets :

$$\begin{aligned}
 |^4\psi_{od} \eta^1(\frac{3}{2})\rangle &= |(^2\Phi_{ov}^{(1)})_o(^3\chi_{od}^{(1)})_a\rangle \\
 &= \{[u_1 \bar{u}_2 v \phi \eta] - [\bar{u}_1 u_2 v \phi \eta]\} / \sqrt{12} \quad \dots (5.9)
 \end{aligned}$$

Doublets :

$$|^2\bar{\psi}_{od} \eta^1(\frac{1}{2})\rangle = \sqrt{\frac{3}{8}} |(^2\Phi_{ov}^{(1)})_o(^3\chi_{od}^{(0)})_a\rangle - \frac{2}{\sqrt{6}} |(^2\Phi_{ov}^{(-1)})_o(^3\chi_{od}^{(1)})_a\rangle \quad (5.10)$$

The explicit form for (5.10) is the same as (5.8) except that the orbital γ is replaced by η .

$$|^2\bar{\psi}_{ov} \eta^1(\frac{1}{2})\rangle = \sqrt{\frac{1}{15}} |(^2\Phi_{od}^{(1)})_o(^3\chi_{od}^{(0)})_a\rangle - \sqrt{\frac{12}{15}} |(^2\Phi_{od}^{(-1)})_o(^3\chi_{od}^{(1)})_a\rangle \quad \dots (5.11)$$

$$\begin{aligned}
 |^2\bar{\psi}_{ee}{}^{\eta_2}(\tfrac{1}{2})\rangle &= \sqrt{\tfrac{2}{5}} |(^4\Phi_{od}(\tfrac{1}{2}))_o(^2\chi_{od}(-1))_e\rangle - \sqrt{\tfrac{2}{5}} |(^4\Phi_{od}(\tfrac{1}{2}))_o(^2\chi_{od}(0))_e\rangle \\
 &\quad + \sqrt{\tfrac{2}{5}} |(^4\Phi_{od}(-\tfrac{1}{2}))_o(^2\chi_{od}(1))_e\rangle \quad \dots \quad (5.12)
 \end{aligned}$$

The explicit forms of (5.11) and (5.12) are respectively obtained by putting the orbital η in place of γ in (5.6) and (5.7).

6. EVALUATION OF THE ENERGY MATRIX

The Hamiltonian (in atomic units $e = \hbar = m = 1$) is

$$H = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_i V(r_i) + \sum_{i,j} \frac{1}{r_{ij}} \quad \dots \quad (6.1)$$

where $V(r_i)$ is the potential acting on the i th electron due to the four nuclei and all other electrons except the five under consideration. The energy matrix of the Hamiltonian within the manifold described in the previous section is given below :

Diagonal elements

Ground states :

$$\langle ^4\bar{\psi}_{od} | H | ^4\bar{\psi}_{od} \rangle = [Q_0 - J(u_1 u_2) - 2J(u_1 v) - 2J(u_1 \phi) - J(v\phi)] \quad \dots \quad (6.2)$$

$$\langle ^2\bar{\psi}_{od} | H | ^2\bar{\psi}_{od} \rangle = [Q_0 - J(u_1 u_2) + J(u_1 v) - 2J(u_1 \phi) - J(v\phi)] \quad \dots \quad (6.3)$$

$$\langle ^2\bar{\psi}_{ee} | H | ^2\bar{\psi}_{ee} \rangle = [Q_0 + J(u_1 u_2) - J(u_1 v) - 2J(u_1 \phi) - J(v\phi)] \quad \dots \quad (6.4)$$

Excited states involving transition to γ type orbital.

Quartets :

$$\begin{aligned}
 \langle ^4\bar{\psi}_{od}{}^{\gamma_1} | H | ^4\bar{\psi}_{od}{}^{\gamma_1} \rangle &= [Q_\gamma - J(u_1 u_2) - 2J(u_1 v) - J(\phi\gamma) \\
 &\quad - \tfrac{1}{2}\{J(u_1 \phi) + J(u_1 \gamma)\} - \tfrac{1}{2}\{J(v\phi) + J(v\gamma)\}] \quad \dots \quad (6.5)
 \end{aligned}$$

$$\begin{aligned}
 \langle ^2\bar{\psi}_{od}{}^{\gamma_2} | H | ^2\bar{\psi}_{od}{}^{\gamma_2} \rangle &= [Q_\gamma - J(u_1 u_2) + J(u_1 v) - J(\phi\gamma) \\
 &\quad - \tfrac{1}{2}\{J(u_1 \phi) + J(u_1 \gamma)\} - \tfrac{1}{2}\{J(v\phi) + J(v\gamma)\}] \quad \dots \quad (6.6)
 \end{aligned}$$

Doublets :

$$\begin{aligned}
 \langle ^2\bar{\psi}_{od}{}^{\gamma_1} | H | ^2\bar{\psi}_{od}{}^{\gamma_1} \rangle &= [Q_\gamma - J(u_1 u_2) + J(u_1 v) - J(\phi\gamma) \\
 &\quad + \tfrac{1}{2}\{J(u_1 \phi) + J(u_1 \gamma)\} - \tfrac{1}{2}\{J(v\phi) + J(v\gamma)\}] \quad \dots \quad (6.7)
 \end{aligned}$$

$$\begin{aligned}
 \langle ^2\bar{\psi}_{od}{}^{\gamma_2} | H | ^2\bar{\psi}_{od}{}^{\gamma_2} \rangle &= [Q_\gamma - J(u_1 u_2) - 2J(u_1 v) - J(\phi\gamma) \\
 &\quad + \tfrac{1}{2}\{2J(u_1 \phi) + 2J(u_1 \gamma) + J(v\phi) + J(v\gamma)\}] \quad \dots \quad (6.8)
 \end{aligned}$$

$$\begin{aligned} \langle {}^2\bar{\psi}_{\sigma\nu}^{\gamma_1} | H | {}^2\bar{\psi}_{\sigma\nu}^{\gamma_1} \rangle &= [Q_\gamma + J(u_1u_2) - J(u_1v) - J(\phi\gamma) \\ &\quad - J(u_1\phi) - J(u_1\gamma) + \frac{1}{2}\{J(v\phi) + J(v\gamma)\}] \end{aligned} \quad (6.9)$$

For transition to η type orbital.

Quartet :

$$\begin{aligned} \langle {}^4\bar{\psi}_{\sigma d}^{\eta_1} | H | {}^4\bar{\psi}_{\sigma d}^{\eta_1} \rangle &= [Q_\eta + J(u_1u_2) - J(u_1v) - J(u_1\phi) - J(u_1\eta) \\ &\quad - J(v\phi) - J(v\eta) - J(\phi\eta)] \end{aligned} \quad (6.10)$$

Doublets :

$$\langle {}^2\bar{\psi}_{\sigma d}^{\eta_1} | H | {}^2\bar{\psi}_{\sigma d}^{\eta_1} \rangle = \text{as in (6.9) with } \gamma \text{ replaced by } \eta. \quad (6.11)$$

$$\langle {}^2\bar{\psi}_{\sigma\nu}^{\eta_1} | H | {}^2\bar{\psi}_{\sigma\nu}^{\eta_1} \rangle = \text{as in (6.7) with } \gamma \text{ replaced by } \eta. \quad (6.12)$$

$$\langle {}^2\bar{\psi}_{\sigma\nu}^{\eta_2} | H | {}^2\bar{\psi}_{\sigma\nu}^{\eta_2} \rangle = \text{as in (6.8) with } \gamma \text{ replaced by } \eta. \quad (6.13)$$

The symbols occurring in the right hand side of Eqns. (6.2) to (6.13) stand for the following :

$$\begin{aligned} Q_0 &= \{2\epsilon_u + \epsilon_v + 2\epsilon_\phi + K(u_1u_2) + 2K(u_1v) + 4K(u_1\phi) \\ &\quad + 2K(v\phi) + K(\phi\phi)\} \end{aligned} \quad (6.14)$$

$$\begin{aligned} Q_a &= \{2\epsilon_u + \epsilon_v + \epsilon_\phi + \epsilon_a + K(u_1u_2) + 2K(u_1v) + 2K(u_1\phi) \\ &\quad + 2K(u_1a) + K(v\phi) + K(va) + K(\phi a)\} \end{aligned} \quad (6.15)$$

$$\left. \begin{aligned} K(ab) &\equiv \langle ab | g_{12} | ab \rangle, \text{ the coulomb integral} \\ J(ab) &\equiv \langle ab | g_{12} | ba \rangle, \text{ the exchange integral} \end{aligned} \right\} \quad (6.16)$$

[see also (6.24)]

$$\text{and } \epsilon_a \equiv \langle a | -\frac{1}{2}\nabla^2 + V | a \rangle \text{ the one electron term.} \quad (6.17)$$

In writing down the final expressions we have made use of the conditions $u_1 \leftrightarrow u_2$ under R_{AM} . It is to be noted that the diagonal matrix elements (6.2) to (6.4) for the zeroth order ground states are degenerate if we neglect the relatively feeble direct exchange integrals such as $J(u_1u_2)$ and $J(u_1v)$. It is essential, therefore, to study the interaction of these states with the corresponding excited states in order to determine the effective coupling on the basis of the present mechanism. The off-diagonal matrix elements will be described now.

Off-diagonal elements

(i) Involving transition to γ .

$$\begin{aligned} \langle {}^4\bar{\psi}_{od} | H | {}^4\bar{\psi}_{od}^{\gamma_1} \rangle &= -\sqrt{\frac{5}{6}} \{ \langle u_1\gamma | g_{12} | \phi u_1 \rangle + \langle u_2\gamma | g_{12} | \phi u_2 \rangle \\ &\quad + \langle v\gamma | g_{12} | \phi v \rangle \} \quad \dots \quad (6.18) \end{aligned}$$

$$\begin{aligned} \langle {}^4\bar{\psi}_{od} | H | {}^4\bar{\psi}_{od}^{\gamma_2} \rangle &= -\sqrt{\frac{1}{6}} \{ \langle u_1\gamma | g_{12} | \phi u_1 \rangle + \langle u_2\gamma | g_{12} | \phi u_2 \rangle \\ &\quad - 2\langle v\gamma | g_{12} | \phi v \rangle \} \quad \dots \quad (6.19) \end{aligned}$$

$$\begin{aligned} \langle {}^2\bar{\psi}_{od} | H | {}^2\bar{\psi}_{od}^{\gamma_1} \rangle &= -\sqrt{\frac{1}{6}} \{ 2\langle u_1\gamma | g_{12} | \phi u_1 \rangle + 2\langle u_2\gamma | g_{12} | \phi u_2 \rangle \\ &\quad - \langle v\gamma | g_{12} | \phi v \rangle \} \quad \dots \quad (6.20) \end{aligned}$$

$$\begin{aligned} \langle {}^2\bar{\psi}_{od} | H | {}^2\bar{\psi}_{od}^{\gamma_2} \rangle &= -\sqrt{\frac{2}{6}} \{ \langle u_1\gamma | g_{12} | \phi u_1 \rangle + \langle u_2\gamma | g_{12} | \phi u_2 \rangle \\ &\quad - 2\langle v\gamma | g_{12} | \phi v \rangle \} \quad \dots \quad (6.21) \end{aligned}$$

$$\langle {}^2\bar{\psi}_{od} | H | {}^2\bar{\psi}_{od}^{\gamma_1} \rangle = \frac{3}{\sqrt{6}} \langle v\gamma | g_{12} | \phi v \rangle \quad \dots \quad (6.22)$$

(ii) For interactions with excited states involving transition to η like orbital, we have one composite expression for the off-diagonal elements, i.e.,

$$\begin{aligned} \langle {}^4\bar{\psi}_{od} | H | {}^4\bar{\psi}_{od}^{\eta_1} \rangle &= \langle {}^2\bar{\psi}_{od} | H | {}^2\bar{\psi}_{od}^{\eta_1} \rangle = \langle {}^2\bar{\psi}_{ev} | H | {}^2\bar{\psi}_{ev}^{\eta_1} \rangle \\ (6.23) \quad &= \frac{1}{\sqrt{2}} \langle {}^2\bar{\psi}_{ev} | H | {}^2\bar{\psi}_{ev}^{\eta_2} \rangle = \frac{1}{\sqrt{2}} \{ \langle u_1\eta | g_{12} | \phi u_1 \rangle \\ &\quad - \langle u_2\eta | g_{12} | \phi u_2 \rangle \} \quad \dots \end{aligned}$$

The notations like $\langle ab | g_{12} | cd \rangle$ in the diagonal and off-diagonal elements represents the integral

$$\int \int a^*(\mathbf{r}_1) b^*(\mathbf{r}_2) \frac{1}{r_{12}} c(\mathbf{r}_1) d(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad \dots \quad (6.24)$$

7. STUDY OF INTERACTION BY PERTURBATION

PROCEDURE

If we examine the diagonal matrix elements of the excited states i.e., Eqns. (6.15) to (6.13) it is seen that the term like $Q(a)$ (explicitly given by (6.15)) is common to all the expressions for transition to 'a' type orbital. Since this contains terms such as the one electron and the coulomb integrals $K(ab)$, it is by far the dominant

term as compared to those involving the exchange integrals $J(ab)$, which are relatively very negligible. We can thus safely use the approximation.

$${}^4E_a \simeq {}^2E_a = E_a' \quad \dots (7.1)$$

where E' represents the mean energy of the excited states involving 'a' orbital. Further, we use the notation

$$E_a = E_a' - E_0 \quad \dots (7.2)$$

where

$${}^4E_0 = {}^2E_0 = E_0$$

i.e., the degenerate energy of the zeroth order ground quartet and doublet states.

As shown in our previous papers (Koide, Sinha and Tanabe, 1959; Sinha and Koide, 1960), the spin dependent energy depressions of the various lower states, within the framework of the present formalism, appears in the second order term of the perturbation treatment. This is expressed as

$$\begin{aligned} \delta E_n &= \sum_n \langle 0 | H | n \rangle \langle n | H | 0 \rangle / (E_n - E_0) \\ &\simeq (E_a)^{-1} \sum_n \langle 0 | H | n \rangle \langle n | H | 0 \rangle \end{aligned} \quad \dots (7.3)$$

using (7.1) and (7.2).

It is expedient to consider certain symmetry situations before giving the explicit expressions for the energy depressions of the various quartet and doublet states based on (7.3).

Under the operation R_{AM} we take, as pointed before, $u_1 \longleftrightarrow u_2$; the behaviour of v either as even or odd function, would not affect the hybrid exchange integrals $\langle vb | g_{12} | cv \rangle$ occurring in the off-diagonal elements. Further, under the operation R_{ON} i.e., reflection on the plane ON normal to the Fig. 1., ϕ is expected to behave as $R_{ON}\phi = -\phi$ because ϕ is either a p_z orbital or a combination of p orbitals by (4.3) depending on the choice of axes. As noted before, for η we take $R_{AM}\eta = -\eta$. In the case of γ , we consider two possibilities.

(a) $R_{AM}\gamma = \gamma$ (always)

(b) i) $R_{ON}\gamma = \gamma$ or ii) $R_{ON}\gamma = -\gamma$.

We shall consider the energy depressions of the states with the condition $R_{ON}\gamma = \gamma$; then we have only to show that the lowest available excited orbital of γ type has this symmetry.

We now consider the explicit expression for the energy depressions of the zeroth order ground states (5.1), (5.2) and (5.3) due to the second order perturba-

tion terms as contained in (7.3), under various conditions. The respective depressions will be symbolically denoted by δQ , δD_1 and δD_2 . These are dealt with casewise.

Case I. (Perturbation by excited states involving transition to γ type orbital).

It is convenient to introduce the following abbreviations

$$\langle u_1\gamma | g_{12} | \phi u_1 \rangle \equiv u_1 J_{\gamma\phi} ; \langle v\gamma | g_{12} | \phi v \rangle \equiv v J_{\gamma\phi} \text{ etc.} \quad \dots (7.4)$$

We also note that $u_2 J_{\gamma\phi} = u_1 J_{\gamma\phi}$ because of the symmetry $u_1 \longleftrightarrow u_2$ under R_{AM} and that $R_{ON} v J_{\gamma\phi} = -v J_{\gamma\phi}$. Thus making use of these conditions in the appropriate off-diagonal elements, the depressions of the various states are expressed below :

$$\delta Q : \{ \frac{5}{6} | (2u_1 J_{\gamma\phi} - v J_{\gamma\phi}) |^2 + \frac{1}{6} | (2u_1 J_{\gamma\phi} + 2v J_{\gamma\phi}) |^2 \} / E_\gamma \quad \dots (7.5)$$

$$\delta D_1 : \{ \frac{1}{6} | (4u_1 J_{\gamma\phi} + v J_{\gamma\phi}) |^2 + \frac{2}{3} | (2u_1 J_{\gamma\phi} + 2v J_{\gamma\phi}) |^2 \} / E_\gamma \quad \dots (7.6)$$

$$\delta D_2 : \frac{1}{6} \{ 9 | v J_{\lambda\phi} |^2 \} / E_\gamma \quad \dots (7.7)$$

It follows, therefore, that

$$\delta Q - \delta D_1 = 6 | u_1 J_{\gamma\phi} | | v J_{\gamma\phi} | / E_\gamma \quad \dots (7.8)$$

$$\delta Q - \delta D_2 = \{ -4 | u_1 J_{\gamma\phi} |^2 + 2 | u_1 J_{\gamma\phi} | | v J_{\gamma\phi} | \} / E_\gamma \quad \dots (7.9)$$

$$\delta D_2 - \delta D_1 = \{ 4 | u_1 J_{\gamma\phi} |^2 + 4 | u_1 J_{\gamma\phi} | | v J_{\gamma\phi} | \} / E_\gamma \quad \dots (7.10)$$

It is easily seen from the above equations that the depression of the D_1 is maximum and it is the lowest of the three states for transition to the γ type orbital. D_2 will probably lie above Q .

Case II. (Involving transition to η type orbital). Noting, $R_{AM} u_1 J_{\eta\phi} = -u_1 J_{\eta\phi}$, the depressions of the various states are :

$$\delta Q : 2 | u_1 J_{\eta\phi} |^2 / E_\eta \quad \dots (7.11)$$

$$\delta D_1 : 2 | u_1 J_{\eta\phi} |^2 / E_\eta \quad \dots (7.12)$$

$$\delta D_2 : \{ 2 | u_1 J_{\eta\phi} |^2 + 4 | u_1 J_{\eta\phi} |^2 \} / E_\eta \quad \dots (7.13)$$

$$\text{Hence} \quad \delta Q - \delta D_1 = 0 \quad \dots (7.14)$$

$$\text{and} \quad \delta Q - \delta D_2 = 4 | u_1 J_{\eta\phi} |^2 / E_\eta \quad \dots (7.15)$$

In this case, D_2 is the lowest state and Q and D_1 lie above and are degenerate. Of the two cases discussed above the fact as to which will dominate would depend on the magnitude of E_γ and E_η as well as the hybrid exchange integrals ${}^a J_{\phi\phi}$ involved. However, it is more appropriate to discuss the case when they are of the same magnitude.

Case III. (The energies of γ and η are equal. We can use the approximation $E_\gamma = E_\eta = E$.) Then we have

$$\delta Q - \delta D_1 = 6 |u_1 J_{\gamma\phi}| |^v J_{\gamma\phi}| / E \quad \dots (7.16)$$

$$\begin{aligned} \delta Q - \delta D_2 &= \{4 |u_1 J_{\eta\phi}|^2 - 4 |u_1 J_{\gamma\phi}|^2 + 2 |u_1 J_{\gamma\phi}| |^v J_{\gamma\phi}|\} / E \\ &\approx 2 |u_1 J_{\gamma\phi}| |^v J_{\gamma\phi}| / E \quad \dots (7.17) \end{aligned}$$

$$\begin{aligned} \delta D_2 - \delta D_1 &= \{4 |u_1 J_{\gamma\phi}|^2 - 4 |u_1 J_{\eta\phi}|^2 + 4 |u_1 J_{\gamma\phi}| |^v J_{\gamma\phi}|\} / E \\ &\approx 4 |u_1 J_{\gamma\phi}| |^v J_{\gamma\phi}| / E \quad \dots (7.18) \end{aligned}$$

assuming that $|u_1 J_{\gamma\phi}| \approx |^v J_{\eta\phi}|$.

If this was the case, then D_1 would be the lowest state, D_2 and Q representing the higher states in respective orders. It may be mentioned again that the ferrimagnetic state D_1 , represents the situation where negative A-B coupling dominates over B-B; D_2 represents the reverse situation. The above analysis shows that the ferro-magnetic state Q is least likely, in agreement with observed cases.

We shall, however, proceed further and investigate deeper into the specific nature of the excited orbitals γ and η available in actual crystals of magnetic spinels and the like systems. After assessing the relative energies of the available excited orbitals, and the magnitude of the hybrid exchange integrals ($^v J_{bc}$), a semi-quantitative discussion of the effective coupling in these systems will be given and compared with results.

8. APPLICATION TO THE REAL SYSTEMS

In order to have a semiquantitative discussion of the model and ideas developed in the preceeding sections as related to spinel-like systems, we shall select a typical representative. Simple examples are $\text{Mn}[\text{Fe}_2]\text{O}_4$ or $\gamma\text{-Fe}_2\text{O}_3$, in which all the cations have d^5 configuration and can be assumed to exist in $^6S_{5/2}$ state.

The first problem is the identification of γ and η type excited orbitals among the lowest available orbitals in the actual crystals. We classify these and ascertain their relative energies with respect to the full unit—A-O-B₃—having C_{3v} symmetry. In discussing the excited orbitals permissible for this point symmetry group, we shall be guided, as before, (Koide, Sinha and Tanabe, 1959), by two models. First we consider the "excitation model" which involves the transition of an electron to the lowest excited orbitals of the anion under the influence of the crystal field of the appropriate symmetry. Second is the charge "transfer model" and describes transitions to such linear combinations of the empty cation orbitals which form base functions of the irreducible representations of the point symmetry group. The lowest lying among these are, of course,

most effective in the transition process (virtual in the present case) being considered here. It may be added that from group theoretical point of view both models represent the same orbitals expressed in slightly different ways of approximations. They should better be termed as localized crystal orbitals.

The excited orbitals of O^{2-} that may be considered on the basis of the "excitation model" are $3s$, $3p$ and $3d$. In order to have a rough estimate of the relative energy scale for these, we consider the effect of the four cations in the unit $A-O-B_3$ (point symmetry C_{3v}) treated as point charges, as well as the twelve oxygen ion neighbours (treated not as point charges but ions with a distribution of charge).

The calculation is carried out by the usual method of crystal field theory (Bethe, 1929; Moffit and Ballhausen, 1956) where the potential is expanded in a series of spherical harmonics, the presence or absence of the terms being governed by the point symmetry group and certain group theoretical ideas. The matrix elements of the potential, thus expressed, were calculated by using the equivalent operator method (Bleaney and Stevens, 1953). The splittings of the orbital levels are proportional to $\langle r^2 \rangle / R^2$, $\langle r^4 \rangle / R^4$ etc., depending on whether the orbital is p -type or d -type. Here ' r ' is the orbital radius and R is the distance of the neighbour in question.

A knowledge of the radial part of the respective wave-functions is needed; however, it is very hard to determine this non-empirically. One can, at best, make a plausible approximation. From the work on excitons for certain systems (Knox and Inchauspe, 1959), it is known that, in the excitation model (Dexter, 1951; 1957) the majority of the charge is confined within the equivalent sphere with its centre at the anion and the surface extending upto the cation centres. Keeping this fact in mind we choose the radial part of the wave-function by the following tentative method.

For example for the $3d$ orbital, we assume that the maximum of the wave-function lies midway between the anion and the cation i.e., for the present case approximately at 2 a.u. distance from the oxygen centre.

In view of the approximations used, it would serve no purpose to give here the details of the calculation. We only enumerate the rough results. Thus, with AO as the z axis and ON as the x axis, we get the following energy sequence :

$$3d_{z^2} < 3d_{xz} = 3d_{yz} \leq 3p_z < 3s < 3p_x = 3p_y < 3d(x^2-y^2) = 3d_{xy}$$

The energy of the $3d_{z^2}$ is lowered by about 6 e.v. with respect to the continuum. It would therefore lie below the conduction band. However, one cannot place too much reliance on the above figure. The important thing is the derived energy sequence and that on the excitation model, a proper choice for γ would be $3d_{z^2}$ orbital and for η $3d_{xz}$. (A different choice of axes will not alter the essen-

tial features; the orbitals will then be the appropriate linear combinations which preserve the symmetry and the sequence). It may be noted, in passing, that $3d_{z^2}$ as γ and $3d_{xz}$ as η satisfy the requisite requirements taken into account in section 7.

We now turn to the charge transfer model in which γ or η are to be constituted out of a linear combination of empty cation orbitals. For the cations considered, we take the $4s$ or orbital or an sp hybrid of the $4s$ and $4p$ orbitals of the respective action having maximum charge density pointing towards the anion and having axial symmetry. We denote them (for the unit A-O-B₃) by σ_t , σ_1 , σ_2 and σ_3 respectively. They form base functions of a reducible representation of dimension 4 for the C_{3v} group. This can be decomposed into the various irreducible representations (for the group theoretical nomenclatures see Landau and Lifshitz, 1958). Thus :

$$\chi\{\Gamma(R)\} = 2\chi(A_1) + \chi(E) \quad \dots \quad (8.1)$$

Accordingly, we have the following combinations :

$$\left. \begin{aligned} \psi_1(A_1) &= \{a_t\sigma_t + a(\sigma_1 + \sigma_2 + \sigma_3)\}/(\text{Normalization}) \\ \psi_2(A_1) &= \{a_t\sigma_t - a(\sigma_1 + \sigma_2 + \sigma_3)\}/(\text{Normalization}) \end{aligned} \right\} \quad \dots \quad (8.2)$$

$$\left. \begin{aligned} \psi_3(E) &= (\sigma_1 - \sigma_2)/\sqrt{2} \\ \psi_4(E) &= (\sigma_1 + \sigma_2 - 2\sigma_3)/\sqrt{6} \end{aligned} \right\} \quad \dots \quad (8.3)$$

Among these some are of no physical interest for the unit A-O-B₂ (Cf. Fig. 1) and we consider only three in the following approximate forms.

$$\psi_a = [\sigma_t + (\sigma_1 + \sigma_2)]/\sqrt{3} \quad (8.4)$$

$$\psi_b = [\sigma_t - (\sigma_1 + \sigma_2)]/\sqrt{3} \quad (8.5)$$

$$\psi_c = [\sigma_1 - \sigma_2]/\sqrt{2} \quad (8.6)$$

Now ψ_c is orthogonal to ϕ ; however, ψ_a and ψ_b are not orthogonal to it. It can be easily seen that the overlap integral of ψ_b with ϕ is much higher than that of ψ_a with ϕ . Thus, the energy of ψ_b is pushed higher up due to mixing with ϕ and the hybrid exchange integral involving it would also be negligible. We can, therefore, safely disregard the effect of ψ_b . Finally, we select ψ_a and ψ_c for γ and η respectively. Since the non-orthogonality of ψ_a with ϕ is negligible, the orbital energies of ψ_a and ψ_c are expected to be nearly equal. Further, the hybrid exchange integrals involving ψ_a and ψ_c will not differ much. This situation leads to the case III dealt with in the Section 7.

It may be emphasised that it is difficult to determine as to which of the two models described above furnish the lowest lying excited orbitals. Since

group-theoretically they are so akin, we shall adopt that model for a semi-quantitative estimate which appeals to our chemical intuition. Accordingly, we choose the charge transfer model and identify γ with ψ_a and η with ψ_s .

The arguments of case III, Section 7 shows that the doublet state D_1 , which represents the state with antiparallel spins in A-B and parallel in B-B lies lowest. D_2 , representing the reverse situation, lies between the quartet Q and D_1 . If we consider the energy level in such a manner that Q represents the zero level, then (7.16) gives the position of D_1 . In the following we give the estimate for the difference $Q-D_1$ in terms of ψ_a and ψ_s i.e., equations (8.4) and (8.6). Thus we have

$$Q-D_1 = 6\{ | \langle u_1 \psi_a | g_{12} | \phi u_1 \rangle | | \langle v \psi_s | g_{12} | \phi v \rangle | \} / E$$

$$\approx 2\{ | \langle u_1 \sigma_1 | g_{12} | \phi u_1 \rangle | | \langle v \sigma_1 | g_{12} | \phi v \rangle | \} / E \quad \dots (8.7)$$

Further, we use p_1 for ϕ , namely $p_1 = \frac{1}{\sqrt{2}}(p_z + p_x)$. The hybrid exchange

integrals of the type $\langle u_1 \sigma | g_{12} | p_z u_1 \rangle$ have been evaluated in the previous paper (Koide, Sinha and Tanabe, 1959) for similar cations and anions. These are of the order of 0.01 a.u. or 0.27 e.v. for the separations involved in spinels. For determining $E \sim (Ea - Eo)$, the ionization potential and electron affinity data for the cation and anions were respectively used. The order is of about 1 a.u. However, for the present purpose, we shall use the range 0.5 to 1.5, a.u., Using these values the difference $\Delta E \equiv Q - D_1$ is set out in Table 1.

TABLE I

E a.u.	ΔE	
	a.u.	$^{\circ}\text{K}$
0.5	4×10^{-4}	125
1.0	2×10^{-4}	62.5
1.5	1.33×10^{-4}	42

A reasonable estimate for $(Q-D_1)$ pertaining to the systems such as $\text{Mn Fe}_2\text{O}_4$ would be around 50°K . The above is for a single representative electron from each cation. No attempt is made to relate this difference with the Curie temperature of the ferrites.

9. DISCUSSION

The purpose of the analysis presented in the foregoing sections has been to explore the nature of indirect exchange interaction for ferros spinels on the basis of the mechanism proposed. The stability of the ferromagnetic and the

two ferrimagnetic states have been studied. It emerges from these considerations that the ferrimagnetic state, symbolized, by D_1 is most stable. In contrast, the ferromagnetic state is least stable. This conclusion is in agreement with Neel's assumption and also the observed situation in most ferrosinels where the negative A-B interaction is the most dominant effect (Gorter, 1954).

It may be pointed, however, that the state symbolised by D_2 (i.e., where B-B are antiparallel and A-B parallel), may become important under certain conditions. If the situation as discussed in Case III of Section 7, prevails, D_2 is more stable compared to the ferromagnetic state Q . However, to ascertain as to when it dominates over D_1 also, a precise knowledge of the excited orbitals is needed. It seems probable that D_2 may become most stable when the cation at the tetrahedral site is in a low spin state as compared to both the cations at the octahedral sites.

This paper does not assess the importance of this mechanism as compared to others. The greatest difficulty for all mechanisms lies in getting an accurate idea of the wave functions of electrons in crystals. Non-empirical calculations are obviously formidable. It is hoped that experiments may eventually resolve some of these difficulties.

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